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Self-healing of deformation damage in underaged Al–Cu–Mg alloys

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The generation and evolution of open volume defects in underaged and T3 Al–Cu–Mg alloy is studied with positron annihilation spectroscopy. During room temperature ageing the positron lifetime in plastically deformed, underaged material approaches the saturation lifetime of the undeformed material. Doppler-broadening results indicate that this behaviour can be attributed to diffusion and clustering of retained solute Cu atoms at the deformation defects, a process of relevance for the introduction of a self-healing mechanism in age-hardenable aluminium alloys.

Keywords: Positron annihilation; Self-healing; Aluminium alloys; Precipitation

Plastic deformation of age-hardenable aluminium alloys leads to the displacement of dislocations through a matrix containing a dense network of precipitates. These displacements must invariably lead to the formation of deformation defects either at the precipitate matrix interface or at the dislocation networks. At higher strain levels the defects link and form cracks, ultimately resulting in the failure of the material. Given the recent interest in the self-healing of materials, and in particular of aluminium alloys [1], we have initiated a study on possible self-healing of deformation defects in a commercial AA2024 alloy at room temperature [2,3]. This is done by comparing the restoration of the deformation damage in a plastically deformed, underaged (UA) material, containing solute atoms in a slightly supersatured state, with that of plastically deformed T3 material. The effect of underageing on the microstructure in Al–Cu alloys after subsequent ageing at lower temperatures has been investigated by Lumley et al. [1]. Transmission electron microscopy (TEM) micrographs revealed a finer dispersion of Guinier–Preston (GP) zones after secondary precipitation of the UA alloy, leading to an enhanced resistance to mechanical loading. The same authors also observed the beneficial effects of underageing on creep properties, and ascribed these to the presence of retained alloying atoms available for further precipitation. Positron annihilation spectroscopy (PAS) is an ideal technique for studying the generation and evolution of deformation-induced defects as it may provide quantitative information about their concentration as well as their immediate chemical neighbourhood [4]. Positrons are effectively trapped at defects associated with open volumes, e.g. vacancies, voids and misfit locations at the precipitate/matrix interface. Upon trapping, the positron annihilates with an electron into two 511 keV gamma quanta after a time period, typically between 100 and 500 ps, which characterizes the positron lifetime. In general, the lifetime increases for positrons trapped at vacancies and other open-volume defects due to the locally reduced overlap of the electron and positron wave function. By measuring the Doppler shift in the energy of the annihilation gamma quanta, information about the momentum distribution of the electrons involved in the annihilation is obtained. The larger shifts are associated with high-momentum core electrons, which have an element specific momentum distribution, and thus give insight in the elemental configuration at the annihilation site. In its simplest form, two parameters (S and W) are derived from the Doppler broadened 511 keV photo peak

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reflecting a one-dimensional projection of the three-dimensional momentum distribution of the annihilating positron–electron pairs. The S (shape) parameter represents annihilations with (low-momentum) valence electrons and is calculated as the ratio of the number of counts in a fixed momentum window ($|p_L| < 3.5 \times 10^{-3}$ $m_o c$) around the centre of the peak to the total counts. Similarly, the W (wing) parameter is obtained from the contribution of annihilations with high-momentum core electrons in the interval $10 \times 10^{-3} m_o c < |p_L| < 30 \times 10^{-3} m_o c$. At a vacancy the probability of annihilations with high-momentum core electrons is locally decreased. This results in a higher S parameter and a lower W parameter value. The parameters can be described as

$$S = f_b S_b + \sum_{i=1}^{N} f_i S_i, \quad (1)$$

with $1 = f_b + \sum_{i=1}^{N} f_i$.

In Eq. (1) S_b and f_b are the (element characteristic) bulk S parameter and fraction reflecting positrons that annihilate in an interstitial position. The parameters indexed i represent annihilations of positrons in other trapped states such as vacancies, voids, precipitate/matrix interface or grain boundaries. A similar equation holds for the W parameter. If only one defect type is present, the measured S and W parameter values fall on a line connecting, in the (S, W) map, the points (S_b, W_b) and (S_d, W_d), where the subscript d stands for the defect. The position on this line is determined by the fraction of positrons trapped at the defects, i.e. $1 - f_b$.

The combination of these two methods, positron lifetime and Doppler broadening, enables one not only to approximate the defect concentration but also to characterize the local chemical environment of the defect.

The PA measurements were performed on a 1 mm thick AA2024 alloy (with a standard composition Al–4.4Cu–1.5Mg–0.6Mn in wt.%) prepared under three different process conditions:

(1) Fully precipitated material (as-received T3 condition) plastically deformed by 3% uniaxial straining at room temperature.

(2) Solutionized samples at 495 °C for 30 min in N_2 gas and quenched into ice water followed by artificial ageing at 195 °C for 5 min to obtain the UA state.

(3) As (2) followed by plastic deformation as in (1).

The PA analysis was started immediately after each of the above treatments. Plastic deformation was applied parallel to the original rolling direction. In addition, the positron annihilation parameters for pure Al, Cu and Mg were measured on three bulk samples.

Positrons were obtained from a standard ^{22}Na source encapsulated between two 7 μm thick kapton foils sandwiched between two identical samples. Contrary to positron parameters obtained using low-energy beams, positrons injected into the sample directly from the ^{22}Na source yield lifetime and Doppler parameters which are averaged over the positron implantation range (approximately 400 μm for Al).

The positron lifetime setup consists of plastic scintillators and photomultiplier tubes coupled to a fast digitizer (2 GS s^{-1}) [5]. After background subtraction and source correction the lifetime spectra were analyzed with the POSFIT-program [6] using a single Gaussian resolution function with a FWHM of 280 ps. For the Doppler-broadening spectroscopy two HPGe detectors for detecting both annihilation photons in time coincidence were used.

The mean positron lifetime measured during ageing at room temperature for the three samples is shown in Figure 1. It is observed that the initial lifetime varies for each of the samples and that the lifetime approaches an asymptotic value for long ageing times. Note that the positron lifetimes at an Al interstitial position and in an Al vacancy are 166 and 246 ps [7], respectively. The measured lifetimes are all in between these two values, indicating that positrons are trapped by open-volume defects. Given the low activation energy for vacancy diffusion in Al and the time needed for collecting each lifetime spectrum (several hours), the vacancies detected here are paired with solute atoms or are trapped by areas which have higher activation energy for vacancy diffusion. The behaviour observed here thus indicates that there are competing positron traps in the material, with a gradual transition from one into another with increasing ageing time.

The lifetime of the UA sample immediately after the quench from UA temperature is approximately 182 ps, a value close to that of a vacancy in a Cu matrix [8,9]. At the ageing temperature of 195 °C the solute has begun to precipitate with the help of vacancies left in the matrix after the solutionizing treatment. However, the ageing procedure is too short to fully complete the vacancy-assisted precipitation, leading to the situation where most of the vacancy defects are captured in precipitates with a high Cu content. A similar result was obtained by Somosa et al. [9] for UA treatments at 180 °C from 30 s to 10 h. Due to the high activation energy for vacancy diffusion in Cu, the vacancies are slowly liberated from the Cu precipitates to the Al matrix, thereby

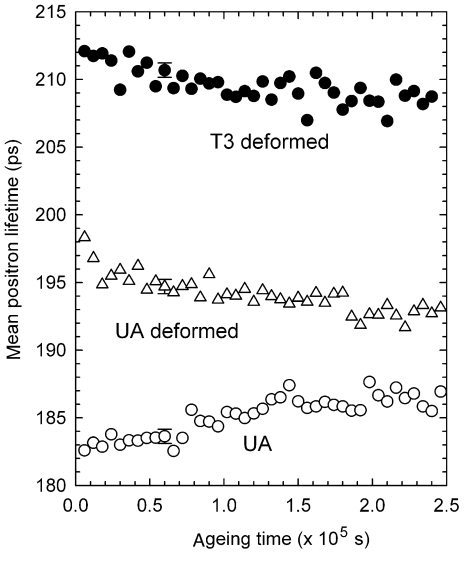

Figure 1. Mean positron lifetime as a function of ageing time at RT for the undeformed underaged (open circles), deformed underaged (open triangles) and deformed T3 (solid circles) samples.

further assisting the diffusion of solute atoms. This may result in an increase of the pre-existing precipitate volume fraction and the formation of new precipitates different from the existing ones [9]. During this process vacancies become available for positron-trapping, which is seen as an increase in lifetime during room temperature (RT) ageing of UA material.

In contrast, a monotonic decrease in the positron lifetime is observed during RT ageing of the UA and fully precipitated samples that have undergone plastic deformation. Such a decrease indicates the disappearance of open-volume defects or a shift in average free volume towards lower values. The positron lifetime measured immediately after the deformation of the fully precipitated material is approximately 15 ps larger than that of the deformed UA material. However, the initial positron lifetime is expected to be the same (212–215 ps) for both systems, which have the same level of straining, but due to the higher initial concentration of solute atoms in combination with the deformation-induced defects, the positron lifetime in the UA sample decreases rapidly. The timescale for this process is apparently much shorter than the time (6000 s) to record the first lifetime spectrum. It is also important to note that after long ageing times the positron lifetime remains 20 ps higher in the deformed T3 alloy in comparison with the deformed UA alloy. At this stage the evolution of the positron lifetime shows the same time dependence, suggesting that the mechanism behind the solute diffusion and precipitation is likely to be the same. Information about the chemical environment of an annihilation site can be obtained from the S and W parameter values, which characterize the electron states at the positron annihilation site. Figure 2 shows the Doppler-broadening data for the low- and high-electron momenta in a (S, W) plot. The lines connect the characteristic positron parameters

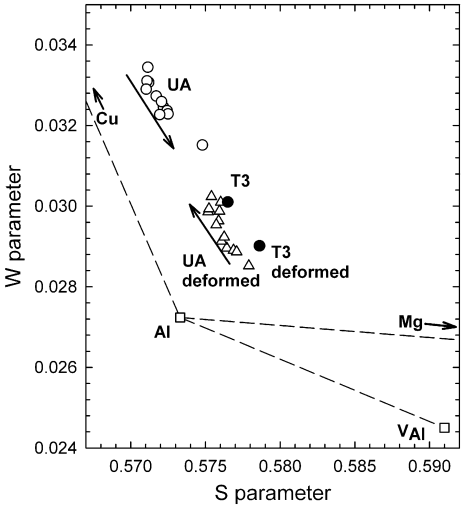

Figure 2. High-momentum parameter W as a function of the low-momentum parameter S for the undeformed underaged (open circles), deformed underaged (open triangles) and deformed T3 (solid circles) samples. The arrows next to the data show the direction of the development of the positron parameters during ageing at RT of the underaged alloy. (Open squares) S, W points for defect-free Al, and an Al vacancy. The location (outside the range of the figure) of the S, W points for Cu and Mg is indicated.

for annihilations in pure Cu, Mg, Al and in an Al vacancy. Note that the characteristic points for Cu and Mg lie far outside the range of the figure. The low S and high W values for Cu are a direct consequence of the overlap of the positron wave function with the Cu 3d electrons. Embedded in an Al matrix, annihilation at sites associated with Cu still gives a recognizable signal and can therefore be easily identified with the help of the (S, W) plot. The two solid symbols in Figure 2 represent the (S, W) values for the fully precipitated T3 material before and after deformation, respectively.

The UA sample without deformation has initial S and W parameters closest to the annihilation parameters for Cu. During ageing the S parameter increases and the W parameter decreases, indicating an increase in annihilations with low-momentum electrons. This is a general trend observed for positron-trapping into vacancy type defects in pure metals where the high-momentum electron density is locally decreased due to the absence of an ion core. In this particular alloy a decrease of W is also expected when positrons are trapped at defects with less overlap with Cu 3d electrons and may form an indication of annihilations at an Al/Mg site at the expense of annihilations associated with Cu.

The annihilation parameters of the UA sample immediately after plastic deformation are the closest to the right-hand lower corner, indicating an increased fraction of annihilations with low-momentum electrons. The straining of the sample has increased the concentration of open-volume defects probed by the positrons. Upon ageing, the W parameter increases, while S parameter decreases. The parameters of UA material after deformation and prolonged ageing at RT are close to those of fully precipitated material before straining. Also, the parameters for the undeformed UA sample approach these values after RT ageing. In addition it is observed that RT ageing of fully precipitated, deformed material does not restore the S and W parameters to their initial values. The overall picture is the same as that derived from the lifetime data: the deformation-induced open volume probed by the positrons is more stable in fully precipitated T3 material as compared to UA material.

To identify separately Cu, Al and Mg with positron annihilation spectroscopy is a very challenging task in commercial Al alloys because even the concentration of minor alloying components is in the upper sensitivity limit of the measurement technique used. While the Cu content is rather high (approximately 2 at.%) the positron parameters in Figure 2 are close to bulk Al values [10]. The positron affinity to Cu in Al is smaller than to Mg, which effectively reduces the signal coming from Cu [11]. However, the situation is different when Cu clusters contain vacancies, which are, regardless of the matrix, very effective positron-trapping sites. After the interrupted UA treatment, these vacancies may be slowly liberated from Cu-rich precipitates and subsequently become trapped at retained solute atoms (Cu or Mg). Since these traps are unstable at RT [9] their concentration decreases during the ageing and they form Cu/Mg co-clusters or GPB zones with vacancies attached. The lifetime associated with these traps is 203 ps [9]. We therefore assume that the observed evolution of the positron lifetime in the undeformed UA

material can be ascribed to an increase of the fraction of positrons annihilating at vacancy defects with a decreased local Cu environment.

The straining of the sample generates dislocations but also vacancies, which diffuse rapidly in the matrix until they are annihilated or trapped by solute atoms, thereby enhancing the atomic diffusion processes. As shown by Detemple et al. [12], the concentration of deformation-induced vacancies depends on strain rate, level of strain and temperature. Above a certain temperature thermally generated vacancies dominate over strain-induced vacancies. By following the same approach, we calculate that the amount of vacancies formed at 495 °C is comparable to the number of vacancies generated by strain at RT. In our experiments, however, the straining was carried out after the UA treatment. Therefore the thermally pre-generated vacancies make only a minor contribution to the rapid decrease of positron lifetime and to solute diffusion because they are already trapped in Cu precipitates before deformation. By assuming that deformation of the UA and T3 material (to the same strain level and at the same strain rate) generates similar dislocation densities and extrinsic vacancy concentrations, we conclude from the observed rapid annihilation of open-volume defects and the overall shorter lifetime during ageing in the strained UA alloys that these effects are not solely due to the interplay between deformation-induced vacancies and dislocations, but require the availability and an enhanced mobility of Cu present in solid solution after UA.

In unstrained UA material the vacancies released by the Cu-rich precipitates play an important role in the diffusion of the atoms still in solid solution. On the other hand, during plastic deformation, dislocations and extrinsic vacancies are generated, which may provide additional means for the rapid diffusion of the solute atoms. On the basis of the results presented here we can only speculate about the mechanism(s) underlying the observed effects. It has been proposed that the dislocation line provides an effective path for (solute) atom diffusion responsible for dynamic strain ageing (DSA). Theoretical calculations [13,14] show that activation energies for solute diffusion along dislocations are still 70–80% of that for vacancy-assisted bulk diffusion. However, this mode of diffusion may become relevant when assisted by the external vacancies introduced by the mechanical deformation of the alloy.

We have studied the generation and room temperature ageing of an UA commercial Al–Cu–Mg-based alloy (AA2024) with PAS in order to explore the possibility of introducing a self-healing mechanism. The positron data measured in the UA Al alloy indicate the existence of positron-trapping sites with high local Cu content. This signal decreases during ageing at RT due to the slow release of vacancies from Cu clusters into the Al matrix. Immediately after plastic deformation the concentration of open-volume defects is high in both the fully precipitated and UA material. During ageing the character of the positron traps is observed to change depending on the thermal pre-treatment of the sample. After long-term ageing at RT the fully precipitated and deformed T3 material has a positron lifetime that is about 20 ps longer than the lifetime of UA material. In contrast to the T3 material, in the UA alloy the rapid initial diffusion of retained solute atoms to the deformation-induced open-volume defects yields final positron parameters close to those of the undeformed alloys. This shows that by interrupting the conventional heat treatment a significant number of solute atoms remains in solution and that these can be driven to and associate with the deformation-induced open-volume defects, a requirement for the successful implementation of self-healing in age-hardenable alloys.

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